

## Suitability of extraction systems with macrocyclic ligands for the study of rutherfordium

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### Introduction

For the first time, the fast, automated liquid-liquid extraction system SISAK was recently successfully used to study the chemical behavior of element 104, rutherfordium [1]. This was made possible by coupling the SISAK system to the Berkeley Gas-filled Separator (BGS). The BGS was used to achieve a physical pre-separation of the desired species from the beam and unwanted reaction products. This pre-separation reduced the background due to the scattered beam and other reaction products substantially and allowed for the detection of rutherfordium atoms without any interference of undesirable activity. The lack of interfering reaction products has several advantages for the design of chemistry experiments with transactinides. In addition to simplifying the detection and data analysis it allows the use of a different class of extraction systems in future SISAK and other chemistry experiments.

The first goal of experiments to study the chemical behavior of transactinide elements is to establish the position of these elements in the periodic table. Then, the properties of the transactinides are systematically compared with those of their lighter homologues and pseudo-homologues to gain further insight into the periodicities within a group of the periodic table and evidence for the influence of relativistic effects. Differences in extraction behavior can be used to differentiate between the individual elements of a group.

In the past, it was necessary to select extraction systems that removed all interfering reaction products and left only the element of interest. Consequently, a very high decontamination factor between the element of interest and interfering activity had to be favored over a high selectivity between the different homologues within the group being studied.

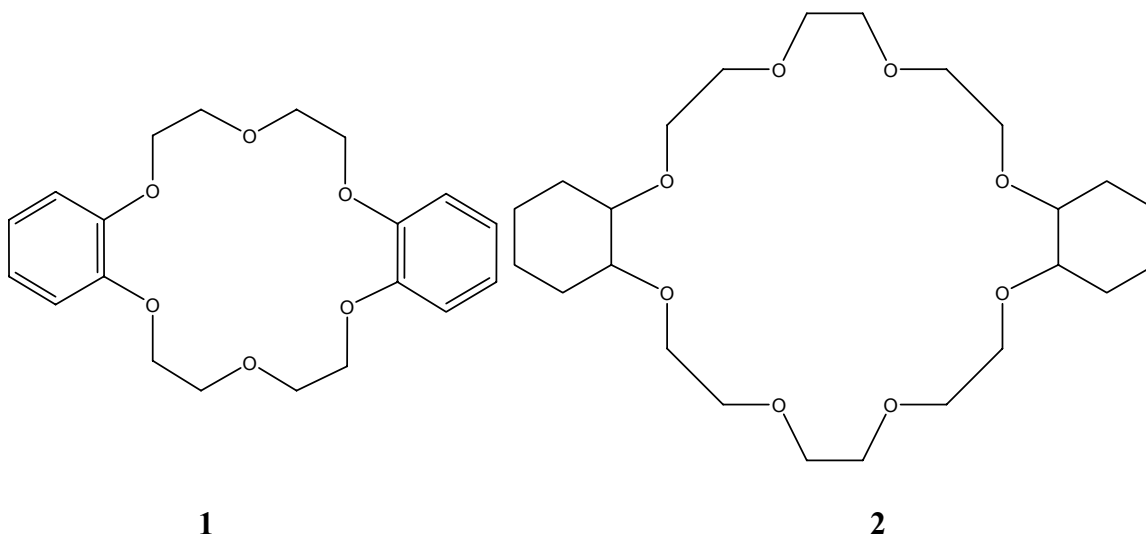
Due to the success of the experiments with pre-separated activity, selectivity between the members of the same group of the periodic table can now be favored over efficient separation from elements belonging to other groups when designing extraction systems for future experiments [2]. This affects the usefulness of extraction systems for the study of transactinide elements and changes their selection criteria. In addition it also gives access to other classes of extraction systems that previously have not been considered when developing solution chemistry experiments.

These additional extraction systems need to be studied regarding their suitability for future experiments with transactinide elements. After the success of the first experiments with pre-separated rutherfordium isotopes, it was decided to start searching for different extraction systems that could be used to study the chemistry of element 104. The extraction systems need not only to be evaluated for their usefulness for future SISAK experiments, but for other automated systems and manual extraction experiments as well.

## Macrocyclic ligands and their application

Several highly selective extractants are currently under investigation in our group, especially systems with macrocyclic ligands.

A macrocyclic ligand can be defined as a compound comprising a ring of at least nine atoms including at least three donor atoms oriented so as to bind to a metal atom. These ligands are a special type of polydentate ligands in which the ligating atoms are constrained in a large ring encircling the metal ion. Examples for such ligands are polyethers in which the ether oxygen atom, separated by two methylene groups each, lie in a nearly planar arrangement about the central metal atom and the remainder of the molecule lies in a “crown” arrangement. All of the oxygen atoms “point” inward toward the metal atom, and these macrocycles form stable complexes with alkali- and other metals [3]. Examples of crown ethers that show promise for experiments with group 4 elements, dibenzo-18-crown-6 (1) and dicyclohexano-24-crown-8 (2), are shown below. Other examples of such macrocyclic ligands include thiacrowns and calixarenes.



The high stability of the complexes of certain metals with macrocyclic ligands and accordingly the high selectivity of such ligands is generally attributed to a size effect. It depends on how closely the metal ion fits into the gap in the center of the ligand. But the differences in complex stability in the gas phase compared to in solution suggest that solvent effects play an important role as well.

The high selectivity of extraction systems with macrocyclic ligands is used in a multitude of applications in analytical and technical chemistry. The coordination chemistry of macrocyclic ligands and alkali and earth alkali metals has been studied in depth [4], and these ligands are most commonly applied for the separation of these metal ions. In addition, these extractants show also promise for the separation of other transition and main group metals [5].

Reaction kinetics is another factor in evaluating the suitability of an extraction system for chemistry with transactinide elements. This factor may even be more important than a high selectivity between the members of a group of the periodic table.

Unfortunately, the size of the organic molecules used as extractants can have a large effect on the kinetics of the reactions. While the time necessary to complete a reaction can be a secondary concern for many applications, it is of great importance for the study

of the transactinide elements. Due to the short half-life of the elements studied it is necessary to choose chemical systems that reach equilibrium as fast as possible. This severely restricts the choice of extraction systems with macrocyclic ligands that can be used for the study of rutherfordium or other transactinide elements. The kinetics of any extraction system that shows promise needs to be studied very thoroughly.

The use of different crown ethers, e.g., dicyclohexano-18-crown-6 and dibenzo-18-crown-6, for the separation of zirconium and hafnium has been reported previously in the literature [6,7]. None of these studies were conducted under conditions that can be applied to the study of rutherfordium.

The usefulness of these extractants in experiments with substantially shorter contact and reaction times needs to be studied. In addition the suitability of other systems needs to be also tested.

## Experimental

In this work the extraction of the lighter homologues and pseudo-homologues of rutherfordium with different macrocyclic ligands from mineral acid solutions was studied using tracer activities with short and medium half-lives.

Offline experiments were performed using  $^{88}\text{Zr}$  ( $T_{1/2} = 83.4$  d) and  $^{175}\text{Hf}$  ( $T_{1/2} = 70.0$  d) as tracer activities. In addition, on-line experiments were performed at the 88-inch cyclotron at LBNL. Short-lived isotopes of Zr and Hf were produced by bombarding a  $^{124}\text{Sn}$  target with an  $^{18}\text{O}^{4+}$  and a  $^{50}\text{Ti}^{11+}$  beam, respectively. The zirconium and hafnium isotopes produced were separated from the beam and interfering reaction products using the BGS. After traveling through the BGS, the products passed through a thin Mylar window into the Recoil Transfer Chamber (RTC) [8]. Inside the RTC, the recoils were stopped in helium and transported to the chemistry setup using a potassium chloride aerosol gas jet.

The aerosols containing the activity were deposited on platinum foils and dissolved in mineral acid of appropriate concentration to conduct the extraction experiments.

The extraction of zirconium and hafnium with different macrocyclic ligands was studied from dilute and concentrated mineral acids, mainly hydrochloric acid. The distribution ratios for the elements were determined as a function of acid and ligand concentration.

The extraction experiments were performed on a time scale relevant for experiments with transactinide elements (< 2 minutes). The kinetics of the reaction was studied by varying the contact time during mixing and the time allowed for phase separation. In addition, the influence of different solvents on the extraction was studied.

The results of these experiments will be presented.

## Acknowledgement:

This work was supported by the Director, Office of Science, Office of High Energy and Nuclear Physics, Division of Nuclear Physics, and the Office of Basic Energy Science, Chemical Science Division, U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

The authors would like to thank C. S. Gong, S. E. Herbison, L. M. Farina, J. M. Schwantes and R. E. Wilson for their invaluable help with the online chemistry experiments at the 88-inch cyclotron.

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